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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/00, 3/386	A1	(11) International Publication Number: WO 95/05442 (43) International Publication Date: 23 February 1995 (23.02.95)
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(54) Title: CELLULASE FABRIC-CONDITIONING COMPOSITIONS (57) Abstract Fabric softening compositions comprising fabric softening active(s) and a cellulase formulated so as to provide limited lower levels of cellulase activity, below about 50 CEVU's per liter of rinse solution, during use conditions of addition to the rinse cycle of machine laundry washing processes. Also a process for machine treatment of fabric, especially cotton fabrics, said process comprising treating fabric during the rinse cycle of a machine washing process with one or more cationic and/or nonionic fabric softening agents and cellulase at a level below about 50 CEVU's per liter of rinse solution.		

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CELLULASE FABRIC-CONDITIONING COMPOSITIONS

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Technical Field

The present invention relates to fabric-conditioning compositions to be used in the rinse cycle of laundry washing processes, in order to impart softness as well as fabric appearance benefits to fabrics.

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The present compositions contain fabric softening active(s) and a cellulase, and are formulated so as to provide limited lower levels of cellulase during normal use conditions of addition to the rinse cycle of machine laundry washing processes.

Background of the Invention

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Fabric conditioning compositions, in particular fabric softening compositions to be used in the rinse cycle of laundry washing processes, are well known. Typically, such compositions contain a water-insoluble quaternary-ammonium fabric softening agent, the most commonly used having been di-long alkyl chain ammonium chloride.

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The anti-harshening effect of cellulase on fabrics is known from e.g. FR 2 481 712 or GB-A-1 368 599, as well as their fabric care benefits, disclosed in e.g. EPA 269 168, all incorporated herein by reference in their entirety. Cellulases have been mainly described however for use in detergent compositions to be used in the main wash cycle of laundry processes, and have found some commercial application in this context.

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In spite of such teachings, the use of cellulases in rinse added fabric softener compositions has apparently not been commercially pursued so far. The reason may be that one of the potential issues to be resolved is to provide acceptable stability of the cellulase in such compositions upon storage. Another reason may be potential issues to be resolved around the effectiveness of cellulase use in the rinse cycle following a normal detergent wash cycle. Such conditions are typically of shorter duration and lower temperatures than used in the wash cycle, and there are concerns around potential for fabric damage if too high activity cellulase conditions

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are met by the rinse cycle use conditions and/or by carry over of cellulase activity from use of cellulase-containing detergents in the wash cycle.

It has been discovered that rinse added fabric softener compositions can be formulated to contain cellulase to provide cellulase activity during normal use conditions to be within certain limits so as to provide fabric softening benefits with an acceptable impact on fabric wear. The present invention therefore allows to formulate fabric softening compositions over the entire typical pH range of fabric softening agents, including pH of 5 to 7 for traditional fabric softening actives, while achieving both effectiveness and fabric safety benefits.

Summary of the Invention

The present invention relates to fabric conditioning compositions comprising one or more cationic and/or nonionic fabric softening agents and a cellulase, said compositions having cellulase present at a level such that the compositions deliver an effective amount of cellulase below about 50 CEVU's per liter of rinse solution during normal washing rinse cycle use conditions.

The present invention further relates to a process for treatment of fabric, especially cotton fabrics, said process comprising treating fabric during the rinse cycle of a washing process with one or more cationic and/or nonionic fabric softening agents and cellulase at a level below about 50 CEVU's per liter of rinse solution.

Detailed Description of the Invention

The cellulase

The cellulase usable in the compositions herein can be any bacterial or fungal cellulase. Suitable cellulases are disclosed, for example, in GB-A-2 075 028, GB-A-2 095 275 and DE-OS-24 47 832, all incorporated herein by reference in their entirety.

Examples of such cellulases are cellulase produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly by the *Humicola* strain DSM 1800, and cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula* Solander).

The cellulase added to the composition of the invention may be in the form of a non-dusting granulate, e.g. "marumes" or "prills", or in the form of a liquid, e.g., one in which the cellulase is provided as a cellulase concentrate suspended in e.g. a nonionic surfactant or dissolved in an aqueous medium.

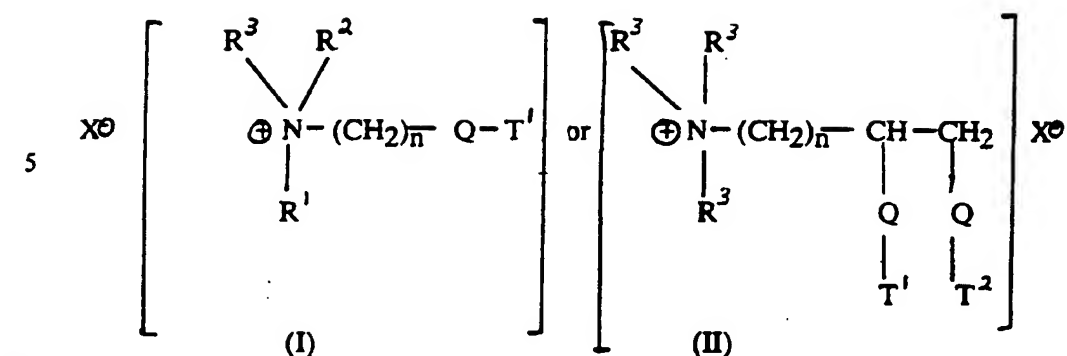
Preferred cellulases for use herein are characterized in that they provide at least 10% removal of immobilized radioactive labelled carboxymethyl-cellulose according to the C¹⁴CMC-method described in EPA 350 098 (incorporated herein by reference in its entirety) at 25x10⁻⁶% by weight of cellulase protein in the laundry test solution.

Most preferred cellulases are those as described in International Patent Application WO91/17243, incorporated herein by reference in its entirety. For example, a cellulase preparation useful in the compositions of the invention can consist essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from Humicola insolens, DSM 1800, or which is homologous to said 43kD endoglucanase.

The cellulases herein should be used in the fabric-conditioning compositions of the present invention at a level equivalent to an activity from about 5 to about 125 CEVU/gram of composition [CEVU=Cellulase (equivalent) Viscosity Unit, as described, for example, in WO 91/13136, incorporated herein by reference in its entirety], and most preferably about 20 to about 100. Such levels of cellulase are selected to provide the critical cellulase activity at a level such that the compositions deliver a fabric softening effective amount of cellulase below about 50 CEVU's per liter of rinse solution, preferably below about 30 CEVU's per liter, more preferably below about 25 CEVU's per liter, and most preferably below about 20 CEVU's per liter, during the rinse cycle of a machine washing process. Preferably, the present invention compositions are used in the rinse cycle at a level to provide from about 5 CEVU's per liter rinse solution to about 50 CEVU's per liter rinse solution, more preferably from about 5 CEVU's per liter to about 30 CEVU's per liter, even more preferably from about 10 CEVU's per liter to about 25 CEVU's per liter, and most preferably from about 10 CEVU's per liter to about 20 CEVU's per liter.

The Cationic or Nonionic Fabric Softening Agents:

The preferred fabric softening agents to be used in the present invention compositions are quaternary ammonium compounds or amine precursors herein having the formula (I) or (II), below :



- Q is $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$ or $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ or $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ or $-\text{NR}^4-\overset{\text{O}}{\parallel}{\text{C}}-$ or $-\overset{\text{O}}{\parallel}{\text{C}}-\text{NR}^4-$;
 R¹ is $(\text{CH}_2)_n-\text{Q}-\text{T}^2$ or T³;
 R² is $(\text{CH}_2)_m-\text{Q}-\text{T}^4$ or T⁵ or R³;
 R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;
 R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;
 T¹, T², T³, T⁴, T⁵ are (the same or different) C₁₁-C₂₂ alkyl or alkenyl;
 n and m are integers from 1 to 4; and
 X⁻ is a softener-compatible anion.

The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowoyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl);
- 3) N,N-di(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 4) N,N-di(2-tallowyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
- 5) N-(2-tallowyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
- 7) N-(2-tallowyloxy-2-oxoethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride); and

8) 1,2-ditallowyl oxy-3-trimethylammoniopropane chloride.;
and mixtures of any of the above materials.

Of these, compounds 1-7 are examples of compounds of Formula (I);
compound 8 is a compound of Formula (II).

5 Particularly preferred is N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl
ammonium chloride, where the tallow chains are at least partially unsaturated.

The level of unsaturation of the tallow chain can be measured by the Iodine
Value (IV) of the corresponding fatty acid, which in the present case should
preferably be in the range of from 5 to 100 with two categories of compounds
10 being distinguished, having a IV below or above 25.

Indeed, for compounds of Formula (I) made from tallow fatty acids having a
IV of from 5 to 25, preferably 15 to 20, it has been found that a cis/trans
isomer weight ratio greater than about 30/70, preferably greater than about
50/50 and more preferably greater than about 70/30 provides optimal
15 concentrability.

For compounds of Formula (I) made from tallow fatty acids having a IV of
above 25, the ratio of cis to trans isomers has been found to be less critical
unless very high concentrations are needed.

Other examples of suitable quaternary ammoniums of Formula (I) and (II)
20 are obtained by, e.g.,

- replacing "tallow" in the above compounds with, for example, coco, palm,
lauryl, oleyl, ricinoleyl, stearyl, palmityl, or the like, said fatty acyl chains being
either fully saturated, or preferably at least partly unsaturated;
- replacing "methyl" in the above compounds with ethyl, ethoxy, propyl,
25 propoxy, isopropyl, butyl, isobutyl or t-butyl;
- replacing "chloride" in the above compounds with bromide, methylsulfate,
formate, sulfate, nitrate, and the like.

In fact, the anion is merely present as a counterion of the positively
charged quaternary ammonium compounds. The nature of the counterion is
30 not critical at all to the practice of the present invention. The scope of this
invention is not considered limited to any particular anion.

By "amine precursors thereof" is meant the secondary or tertiary amines
corresponding to the above quaternary ammonium compounds, said amines
being substantially protonated in the present compositions due to the claimed
35 pH values.

The quaternary ammonium or amine precursors compounds herein are
present at levels of from about 1% to about 80% of compositions herein,
depending on the composition execution which can be dilute with a preferred

level of active from about 5% to about 15%, or concentrated, with a preferred level of active from about 15% to about 50%, most preferably about 15% to about 35%.

5 For the preceding fabric softening agents, the pH of the compositions herein is an essential parameter of the present invention. Indeed, it influences the stability of the quaternary ammonium or amine precursors compounds, and of the cellulase, especially in prolonged storage conditions.

10 The pH, as defined in the present context, is measured in the neat compositions, in the continuous phase after separation of the dispersed phase by ultra centrifugation, at 20°C. For optimum hydrolytic stability of these compositions, the neat pH, measured in the above-mentioned conditions, must be in the range of from about 2.0 to about 4.5, preferably about 2.0 to about 3.5. The pH of these compositions herein can be
15 regulated by the addition of a Bronsted acid.

Examples of suitable acids include the inorganic mineral acids, carboxylic acids, in particular the low molecular weight (C₁-C₅) carboxylic acids, and alkylsulfonic acids. Suitable inorganic acids include HCl, H₂SO₄, HNO₃ and H₃PO₄. Suitable organic acids include formic, acetic,
20 citric, methylsulfonic and ethylsulfonic acid. Preferred acids are citric, hydrochloric, phosphoric, formic, methylsulfonic acid, and benzoic acids.

Softening agents also useful in the present invention compositions are nonionic fabric softener materials, preferably in combination with cationic softening agents. Typically, such nonionic fabric softener
25 materials have a HLB of from about 2 to about 9, more typically from about 3 to about 7. Such nonionic fabric softener materials tend to be readily dispersed either by themselves, or when combined with other materials such as single-long-chain alkyl cationic surfactant described in detail hereinafter. Dispersibility can be improved by using more single-long-chain
30 alkyl cationic surfactant, mixture with other materials as set forth hereinafter, use of hotter water, and/or more agitation. In general, the materials selected should be relatively crystalline, higher melting, (e.g. >40°C) and relatively water-insoluble.

35 The level of optional nonionic softener in the compositions herein is typically from about 0.1% to about 10%, preferably from about 1% to about 5%.

Preferred nonionic softeners are fatty acid partial esters of polyhydric alcohols, or anhydrides thereof, wherein the alcohol, or

anhydride, contains from 2 to 18, preferably from 2 to 8, carbon atoms, and each fatty acid moiety contains from 12 to 30, preferably from 16 to 20, carbon atoms. Typically, such softeners contain from one to 3, preferably 2 fatty acid groups per molecule.

5 The polyhydric alcohol portion of the ester can be ethylene glycol, glycerol, poly (e.g., di-, tri-, tetra, penta-, and/or hexa-) glycerol, xylitol, sucrose, erythritol, pentaerythritol, sorbitol or sorbitan. Sorbitan esters and polyglycerol monostearate are particularly preferred.

10 The fatty acid portion of the ester is normally derived from fatty acids having from 12 to 30, preferably from 16 to 20, carbon atoms, typical examples of said fatty acids being lauric acid, myristic acid, palmitic acid, stearic acid and behenic acid.

15 Highly preferred optional nonionic softening agents for use in the present invention are the sorbitan esters, which are esterified dehydration products of sorbitol, and the glycerol esters.

Commercial sorbitan monostearate is a suitable material. Mixtures of sorbitan stearate and sorbitan palmitate having stearate/palmitate weight ratios varying between about 10:1 and about 1:10, and 1,5-sorbitan esters are also useful.

20 Glycerol and polyglycerol esters, especially glycerol, diglycerol, triglycerol, and polyglycerol mono- and/or di-esters, preferably mono-, are preferred herein (e.g. polyglycerol monostearate with a trade name of Radasurf 7248).

25 Useful glycerol and polyglycerol esters include mono-esters with stearic, oleic, palmitic, lauric, isostearic, myristic, and/or behenic acids and the diesters of stearic, oleic, palmitic, lauric, isostearic, behenic, and/or myristic acids. It is understood that the typical mono-ester contains some di- and tri-ester, etc.

30 The "glycerol esters" also include the polyglycerol, e.g., diglycerol through octaglycerol esters. The polyglycerol polyols are formed by condensing glycerin or epichlorohydrin together to link the glycerol moieties via ether linkages. The mono- and/or diesters of the polyglycerol polyols are preferred, the fatty acyl groups typically being those described hereinbefore for the sorbitan and glycerol esters.

35 Additional fabric softening agents useful herein are described in U.S. Pat. No. 4,661,269, issued April 28, 1987, in the names of Toan Trinh, Errol H. Wahi, Donald M. Swartley, and Ronald L. Hemingway; U.S. Pat. No. 4,439,335, Burns, issued March 27, 1984;

and in U.S. Pat. Nos.: 3,861,870, Edwards and Diehl; 4,308,151, Cambre; 3,886,075, Bernardino; 4,233,164, Davis; 4,401,578, Verbruggen; 3,974,076, Wiersema and Rieke; and 4,237,016, Rudkin, Clint, and Young, all of said patents being incorporated herein by reference.

For example, suitable fabric softener agents useful herein may comprise one, two, or all three of the following fabric softening agents:

(a) the reaction product of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof (preferably from about 10% to about 80%); and/or

(b) cationic nitrogenous salts containing only one long chain acyclic aliphatic C₁₅-C₂₂ hydrocarbon group (preferably from about 3% to about 40%); and/or

(c) cationic nitrogenous salts having two or more long chain acyclic aliphatic C₁₅-C₂₂ hydrocarbon groups or one said group and an arylalkyl group (preferably from about 10% to about 80%);

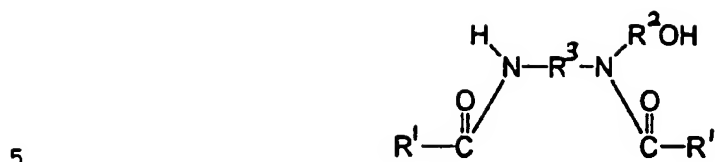
with said (a), (b) and (c) preferred percentages being by weight of the fabric softening agent component of the present invention compositions.

Following are the general descriptions of the preceeding (a), (b), and (c) softener ingredients (including certain specific examples which illustrate, but do not limit the present invention).

Component (a): Softening agents (actives) of the present invention may be the reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof. These reaction products are mixtures of several compounds in view of the multi-functional structure of the polyamines.

The preferred Component (a) is a nitrogenous compound selected from the group consisting of the reaction product mixtures or some selected components of the mixtures. More specifically, the preferred Component (a) is compounds selected from the group consisting of:

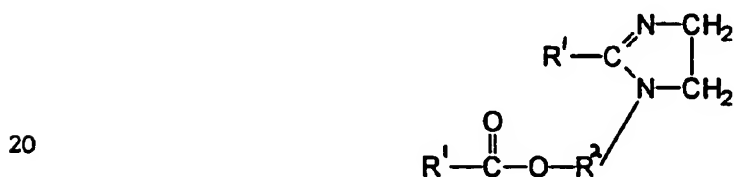
(i) the reaction product of higher fatty acids with hydroxy alkylalkylenediamines in a molecular ratio of about 2:1, said reaction product containing a composition having a compound of the formula:



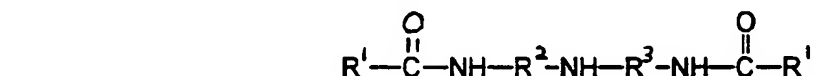
wherein R¹ is an acyclic aliphatic C₁₅-C₂₁ hydrocarbon group and R² and R³ are divalent C₁-C₃ alkylene groups;
 (ii) substituted imidazoline compounds having the formula:



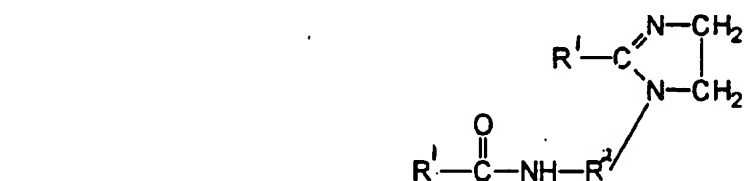
wherein R¹ and R² are defined as above;
 (iii) substituted imidazoline compounds having the formula:



wherein R¹ and R² are defined as above;
 (iv) the reaction product of higher fatty acids with dialkylenetriamines in a molecular ratio of about 2:1, said reaction product containing a composition having a compound of the formula:



wherein R¹, R² and R³ are defined as above; and
 (v) substituted imidazoline compounds having the formula:



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wherein R¹ and R² are defined as above; and
 (vi) mixtures thereof.

Component (a)(i) is commercially available as Mazamide® 6, sold by Mazer Chemicals, or Ceranine® HC, sold by Sandoz Colors & Chemicals; here the higher fatty acids are hydrogenated tallow fatty acids and the hydroxyalkylalkylenediamine is N-2-hydroxyethylethylenediamine, and R¹ is an aliphatic C₁₅-C₁₇ hydrocarbon group, and R² and R³ are divalent ethylene groups.

An example of Component (a)(ii) is stearic hydroxyethyl imidazoline wherein R¹ is an aliphatic C₁₇ hydrocarbon group, R² is a divalent ethylene group; this chemical is sold under the trade names of Alkazine® ST by Alkaril Chemicals, Inc., or Schercozoline® S by Scher Chemicals, Inc.

An example of Component (a)(iv) is N,N"-ditallowalkoyldiethylenetriamine where R¹ is an aliphatic C₁₅-C₁₇ hydrocarbon group and R² and R³ are divalent ethylene groups.

An example of Component (a)(v) is 1-tallowamidoethyl-2-tallowimidazoline wherein R¹ is an aliphatic C₁₅-C₁₇ hydrocarbon group and R² is a divalent ethylene group.

The Components (a)(iii) and (a)(v) can also be first dispersed in a Bronsted acid dispersing aid having a pKa value of not greater than about 4; provided that the pH of the final composition is not greater than about 5. Some preferred dispersing aids are hydrochloric acid, phosphoric acid, or methanesulfonic acid.

Both N,N"-ditallowalkoyldiethylenetriamine and 1-tallow(amido ethyl)-2-tallowimidazoline are reaction products of tallow fatty acids and diethylenetriamine, and are precursors of the cationic fabric softening agent methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate (see "Cationic Surface Active Agents as Fabric Softeners," R. R. Egan, Journal of the American Oil Chemicals' Society, January 1978, pages 118-121). N,N"-ditallow alkoyldiethylenetriamine and 1-tallowamidoethyl-2-tallowimidazoline can be obtained from Witco Chemical Company as experimental chemicals. Methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is sold by Witco Chemical Company under the tradename Varisoft® 475.

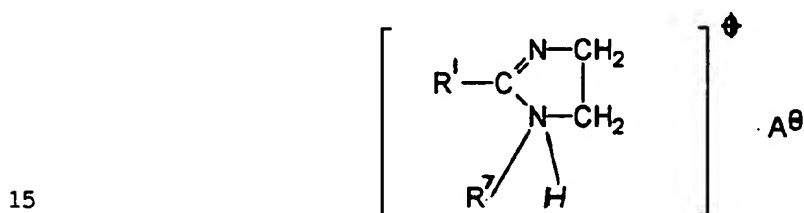
Component (b) : The preferred Component (b) is a cationic nitrogenous salt containing one long chain acyclic aliphatic C₁₅-C₂₂ hydrocarbon group selected from the group consisting of:

(i) acyclic quaternary ammonium salts having the formula:



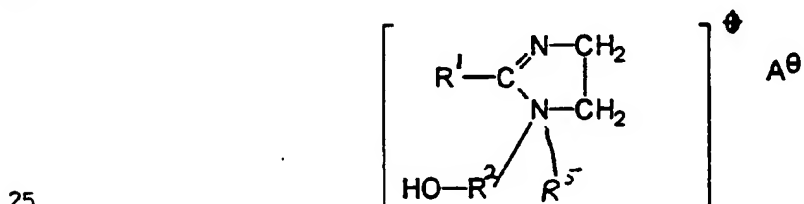
wherein R^4 is an acyclic aliphatic C_{15} - C_{22} hydrocarbon group, R^5 and R^6 are C_1 - C_4 saturated alkyl or hydroxy alkyl groups, and A^- is an anion;

(ii) substituted imidazolinium salts having the formula:



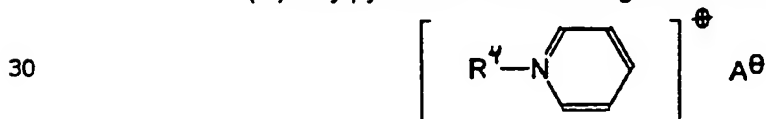
wherein R^1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon group, R^7 is a hydrogen or a C_1 - C_4 saturated alkyl or hydroxyalkyl group, and A^- is an anion;

(iii) substituted imidazolinium salts having the formula:



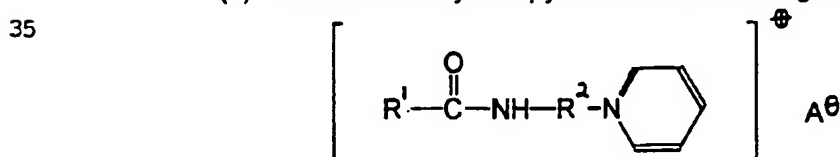
wherein R^2 is a divalent C_1 - C_3 alkylene group and R^1 , R^5 and A^- are as defined above;

(iv) alkylpyridinium salts having the formula:



wherein R^4 is an acyclic aliphatic C_{16} - C_{22} hydrocarbon group and A^- is an anion; and

(v) alkanamide alkylene pyridinium salts having the formula:



wherein R^1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon group, R^2 is a divalent C_1 - C_3 alkylene group, and A- is an ion group;

(vi) monoester quaternary ammonium compounds having the formula:

5 $[(R)_3 - N^+ - (CH_2)_n - Y - R^2] A^-$
 wherein
 each Y = $-O-(O)C-$, or $-C(O)-O-$;
 each n = 1 to 4;

each R substituent is a short chain C_1 - C_6 , preferably C_1 - C_3 alkyl
 10 or hydroxyalkyl group, e.g., methyl (most preferred), ethyl, propyl, hydroxyethyl, and the like, benzyl or mixtures thereof;

R^2 is a long chain C_{10} - C_{22} hydrocarbyl, or substituted hydrocarbyl substituent, preferably C_{15} - C_{19} alkyl and/or alkenyl, most preferably C_{15} - C_{18} straight chain alkyl and/or alkenyl; and

15 the counterion, A-, can be any softener-compatible anion, for example, chloride, bromide, methylsulfate, formate, sulfate, nitrate and the like; and

(vii) mixtures thereof.

Examples of Component (b)(i) are the

20 monoalkyltrimethylammonium salts such as monotallowtrimethylammonium chloride, mono(hydrogenated tallow)trimethylammonium chloride, palmityltrimethyl ammonium chloride and soyatrimethylammonium chloride, sold by Sherex Chemical Company under the trade name Adogen® 471, Adogen® 441, Adogen®
 25 444, and Adogen® 415, respectively. In these salts, R^4 is an acyclic aliphatic C_{16} - C_{18} hydrocarbon group, and R^5 and R^6 are methyl groups. Mono(hydrogenated tallow)trimethylammonium chloride and monotallowtrimethylammonium chloride are preferred.

Other examples of Component (b)(i) are

30 behenyltrimethylammonium chloride wherein R^4 is a C_{22} hydrocarbon group and sold under the trade name Kemamine® Q2803-C by Humko Chemical Division of Witco Chemical Corporation; soyadimethylethylammonium ethylsulfate wherein R^4 is a C_{16} - C_{18} hydrocarbon group, R^5 is a methyl group, R^6 is an ethyl group, and A-
 35 is an ethylsulfate anion, sold under the trade name Jordaqat® 1033 by Jordan Chemical Company; and methyl-bis(2-hydroxyethyl)-octadecylammonium chloride wherein R^4 is a C_{18} hydrocarbon group,

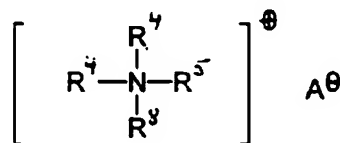
R⁵ is a 2-hydroxyethyl group and R⁶ is a methyl group and available under the trade name Ethoquad® 18/12 from Armac Company.

An example of Component (b)(iii) is 1-ethyl-1-(2-hydroxyethyl)-2-isoheptadecylimidazolinium ethylsulfate wherein R¹ is a C₁₇ hydrocarbon group, R² is an ethylene group, R⁵ is an ethyl group, and A⁻ is an ethylsulfate anion. It is available from Mona Industries, Inc., under the trade name Monaquat® ISIES.

An example of Component (b)(vi) is mono(tallowoyloxyethyl)hydroxyethyltrimethylammonium chloride, i.e., monoester of tallow fatty acid with di(hydroxyethyl)dimethylammonium chloride, a by-product in the process of making diester of tallow fatty acid with di(hydroxyethyl)dimethylammonium chloride, i.e., di(tallowoyloxyethyl)dimethylammonium chloride, a (c)(vii) component (vide infra).

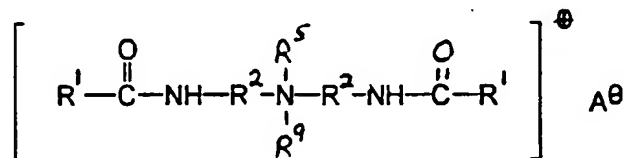
Component (c) : Preferred cationic nitrogenous salts having two or more long chain acyclic aliphatic C₁₅-C₂₂ hydrocarbon groups or one said group and an arylalkyl group which can be used either alone or as part of a mixture are selected from the group consisting of:

(i) acyclic quaternary ammonium salts having the formula:



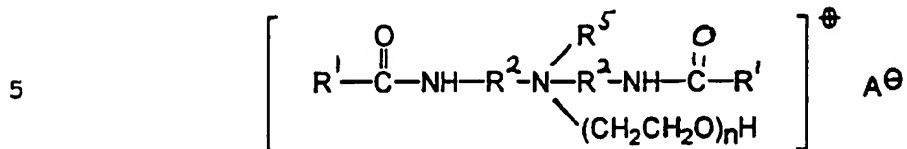
wherein R⁴ is an acyclic aliphatic C₁₅-C₂₂ hydrocarbon group, R⁵ is a C₁-C₄ saturated alkyl or hydroxyalkyl group, R⁶ is selected from the group consisting of R⁴ and R⁵ groups, and A⁻ is an anion defined as above;

(ii) diamido quaternary ammonium salts having the formula:



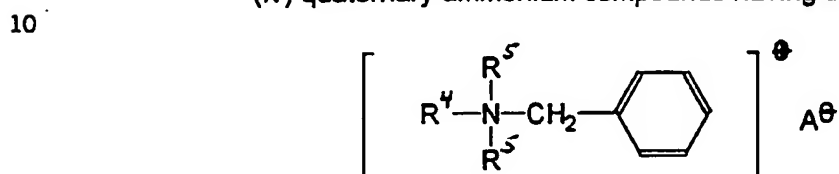
wherein R¹ is an acyclic aliphatic C₁₅-C₂₁ hydrocarbon group, R² is a divalent alkylene group having 1 to 3 carbon atoms, R⁵ and R⁶ are C₁-C₄ saturated alkyl or hydroxyalkyl groups, and A⁻ is an anion;

(iii) diamino alkoxyated quaternary ammonium salts having the formula:



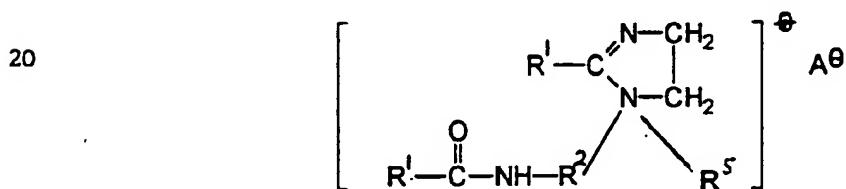
wherein n is equal to 1 to about 5, and R¹, R², R⁵ and A⁻ are as defined above;

(iv) quaternary ammonium compounds having the formula:



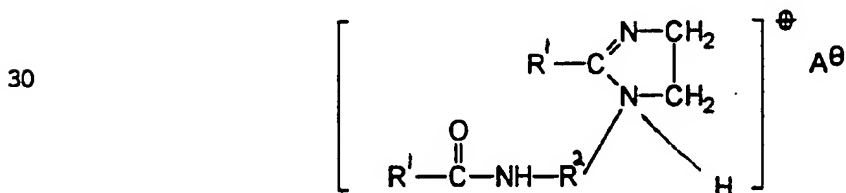
wherein R⁴ is an acyclic aliphatic C₁₅-C₂₂ hydrocarbon group, R⁵ is a C₁-C₄ saturated alkyl or hydroxyalkyl group, A⁻ is an anion;

(v) substituted imidazolinium salts having the formula:



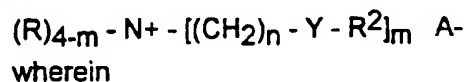
wherein R¹ is an acyclic aliphatic C₁₅-C₂₁ hydrocarbon group, R² is a divalent alkylene group having 1 to 3 carbon atoms, and R⁵ and A⁻ are as defined above; and

(vi) substituted imidazolinium salts having the formula:



wherein R¹, R² and A⁻ are as defined above;

(vii) diester quaternary ammonium (DEQA) compounds having the formula:



each Y = -O-(O)C-, or -C(O)-O-;

m = 2 or 3;

each n = 1 to 4;

5 each R substituent is a short chain C₁-C₆, preferably C₁-C₃ alkyl or hydroxyalkyl group, e.g., methyl (most preferred), ethyl, propyl, hydroxyethyl, and the like, benzyl, or mixtures thereof;

each R² is a long chain C₁₀-C₂₂ hydrocarbyl, or substituted hydrocarbyl substituent, preferably C₁₅-C₁₉ alkyl and/or alkenyl, most preferably C₁₅-C₁₈ straight chain alkyl and/or alkenyl; and
10 the counterion, A-, can be any softener-compatible anion, for example, chloride, bromide, methylsulfate, formate, sulfate, nitrate and the like; and

(viii) mixtures thereof.

Examples of Component (c)(i) are the well-known
15 dialkyldi methylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methylsulfate, di(hydrogenated tallow)di methylammonium chloride, distearyldimethylammonium chloride, dibehenyldimethylammonium chloride. Di(hydrogenated tallow)di methylammonium chloride and ditallowdimethylammonium
20 chloride are preferred. Examples of commercially available dialkyldimethyl ammonium salts usable in the present invention are di(hydrogenated tallow)dimethylammonium chloride (trade name Adogen® 442), ditallowdimethylammonium chloride (trade name Adogen® 470), distearyl dimethylammonium chloride (trade name Arosurf® TA-100), all available from Witco Chemical Company.
25 Dibehenyldimethylammonium chloride wherein R⁴ is an acyclic aliphatic C₂₂ hydrocarbon group is sold under the trade name Kemamine Q-2802C by Humko Chemical Division of Witco Chemical Corporation.

30 Examples of Component (c)(ii) are methylbis(tallowamido ethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate wherein R¹ is an acyclic aliphatic C₁₅-C₁₇ hydrocarbon group, R² is an ethylene group, R⁵ is a
35 methyl group, R⁹ is a hydroxyalkyl group and A- is a methylsulfate anion; these materials are available from Witco Chemical Company under the trade names Varisoft® 222 and Varisoft® 110, respectively.

An example of Component (c)(iv) is dimethylstearylbenzyl ammonium chloride wherein R^4 is an acyclic aliphatic C_{18} hydrocarbon group, R^5 is a methyl group and A^- is a chloride anion, and is sold under the trade names Varisoft® SDC by
 5 Witco Chemical Company and Ammonyx® 490 by Onyx Chemical Company.

Examples of Component (c)(v) are 1-methyl-1-tallowamido ethyl-2-tallowimidazolinium methylsulfate and 1-methyl-1-(hydrogenated tallowamidoethyl)-2-(hydrogenated tallow)imidazolinium
 10 methylsulfate wherein R^1 is an acyclic aliphatic C_{15} - C_{17} hydrocarbon group, R^2 is an ethylene group, R^5 is a methyl group and A^- is a chloride anion; they are sold under the trade names VarisoftR 475 and VarisoftR 445, respectively, by Witco Chemical Company.

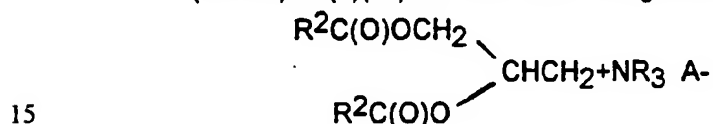
It will be understood that for (c)(vii) above substituents R
 15 and R^2 can optionally be substituted with various groups such as alkoxyl or hydroxyl groups, and/or can be saturated, unsaturated, straight, and/or branched so long as the R^2 groups maintain their basically hydrophobic character. Preferred softening compounds are biodegradable such as those in Component (c)(vii). These preferred
 20 compounds can be considered to be diester variations of ditallow dimethyl ammonium chloride (DTDMAC), which is a widely used fabric softener.

The following are non-limiting examples of (c)(vii) (wherein all long-chain alkyl substituents are straight-chain):
 25 $[CH_3]_2^+ N[CH_2CH_2OC(O)R^2] Cl^-$
 $[HOCH(CH_3)CH_2][CH_3]^+ N[CH_2CH_2OC(O)C_{15}H_{31}]_2 Br^-$
 $[C_2H_5]_2^+ N[CH_2CH_2OC(O)C_{17}H_{35}]_2 Cl^-$
 $[CH_3][C_2H_5]^+ N[CH_2CH_2OC(O)C_{13}H_{27}]_2 I^-$
 $[C_3H_7][C_2H_5]^+ N[CH_2CH_2OC(O)C_{15}H_{31}]_2 ^-SO_4CH_3$
 30 $[CH_3]_2^+ N-CH_2CH_2OC(O)C_{15}H_{31} Cl^-$

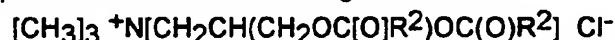
|
 $CH_2CH_2OC(O)C_{17}H_{35}$
 $[CH_2CH_2OH][CH_3]^+ N[CH_2CH_2OC(O)R^2]_2 Cl^-$
 where $-C(O)R^2$ is derived from soft tallow and/or hardened
 35 tallow fatty acids. Especially preferred is diester of soft and/or hardened tallow fatty acids with di(hydroxyethyl)dimethylammonium chloride, also called di(tallowoyloxyethyl)dimethylammonium chloride.

Since the foregoing compounds (diesters) are somewhat labile to hydrolysis, they should be handled rather carefully when used to formulate the compositions herein. For example, stable liquid compositions herein are formulated at a pH in the range of about 2 to about 5, preferably from about 2 to about 4.5, more preferably from about 2 to about 4. The pH can be adjusted by the addition of a Bronsted acid. Ranges of pH for making stable softener compositions containing diester quaternary ammonium fabric softening compounds are disclosed in U.S. Pat. No. 4,767,547, Straathof and Konig, issued Aug. 30, 1988, and is incorporated herein by reference.

The diester quaternary ammonium fabric softening compound (DEQA) of (c)(vii) can also have the general formula:



wherein each R, R², and A- have the same meanings as before. Such compounds include those having the formula:



where -OC(O)R² is derived from soft tallow and/or hardened tallow fatty acids.

Preferably each R is a methyl or ethyl group and preferably each R² is in the range of C₁₅ to C₁₉. Degrees of branching, substitution and/or non-saturation can be present in the alkyl chains. The anion A- in the molecule is preferably the anion of a strong acid and can be, for example, chloride, bromide, sulphate, and methyl sulphate; the anion can carry a double charge in which case A- represents half a group. These compounds, in general, are more difficult to formulate as stable concentrated liquid compositions.

These types of compounds and general methods of making them are disclosed in U.S. Pat. No. 4,137,180, Naik et al., issued Jan. 30, 1979, which is incorporated herein by reference.

A preferred composition contains Component (a) at a level of from about 10% to about 80%, Component (b) at a level of from about 3% to about 40%, and Component (c) at a level of from about 10% to about 80%, by weight of the fabric softening component of the present invention compositions. A more preferred composition contains Component (c) which is selected from the group consisting of: (i) di(hydrogenated tallow)dimethylammonium chloride; (v) methyl-1-

tallowamidoethyl-2-tallowimidazolinium methylsulfate; (vii) diethanol ester dimethylammonium chloride; and mixtures thereof.

An even more preferred composition contains Component (a): the reaction product of about 2 moles of hydrogenated tallow fatty acids with about 1 mole of N-2-hydroxyethylethylenediamine and is present at a level of from about 20% to about 70% by weight of the fabric softening component of the present invention compositions; Component (b): mono(hydrogenated tallow)trimethyl ammonium chloride present at a level of from about 3% to about 30% by weight of the fabric softening component of the present invention compositions; Component (c): selected from the group consisting of di(hydrogenated tallow)dimethylammonium chloride, ditallowdimethylammonium chloride, methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate, diethanol ester dimethylammonium chloride, and mixtures thereof; wherein Component (c) is present at a level of from about 20% to about 60% by weight of the fabric softening component of the present invention compositions; and wherein the weight ratio of said di(hydrogenated tallow)dimethylammonium chloride to said methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is from about 2:1 to about 6:1.

The above individual components can also be used individually, especially those of I(c) (e.g., ditallowdimethylammonium chloride or diethanol ester dimethylammonium chloride).

In the cationic nitrogenous salts described hereinbefore; the anion A⁻ provides charge neutrality. Most often, the anion used to provide charge neutrality in these salts is a halide, such as chloride or bromide. However, other anions can be used, such as methylsulfate, ethylsulfate, hydroxide, acetate, formate, citrate, sulfate, carbonate, and the like. Chloride and methylsulfate are preferred herein as anion A⁻.

The amount of fabric softening agent (fabric softener) in liquid compositions of this invention is typically from about 2% to about 50%, preferably from about 4% to about 30%, by weight of the composition. The lower limits are amounts needed to contribute effective fabric softening performance when added to laundry rinse baths in the manner which is customary in home laundry practice. The higher limits are suitable for concentrated products which provide the

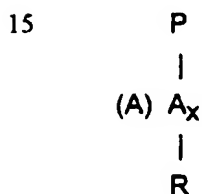
consumer with more economical usage due to a reduction of packaging and distributing costs.

Optional Ingredients

5 Fully formulated fabric softening compositions preferably contain, in addition to the hereinbefore described components, one or more of the following ingredients:

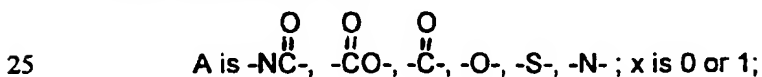
10 Firstly, the presence of polymer having a partial or net cationic charge, can be useful to further increase the cellulase stability in the compositions herein. Such polymers can be used at levels of from 0.001% to 10%, preferably 0.01% to 2% by weight of the compositions.

Such polymers having a partial cationic charge can be polyamine N-oxide containing polymers which contain units having the following structure formula (A):



20

wherein P is a polymerisable unit, whereto the R-N→O group can be attached to or wherein the R-N→O group forms part of the polymerisable unit or a combination of both.

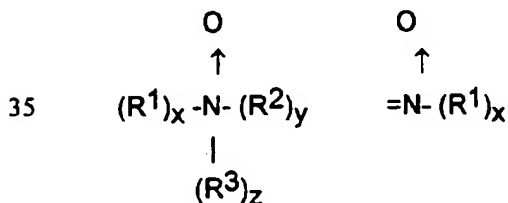


25

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N→O group can be attached or wherein the nitrogen of the N→O group is part of these groups.

30

The N→O group can be represented by the following general structures :



35

wherein R¹, R², and R³ are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N→O group can be attached or wherein the nitrogen of the N→O group forms part of these groups.

- 5 The N→O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N→O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

- 10 One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N→O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

- 15 Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N→O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides where to the N→O group is attached to the polymerisable unit.

- 20 Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (A) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N→O functional group is part of said R group.

- 25 Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

- 30 Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (A) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N→O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties.

- 35 Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers useful herein typically have a ratio of amine to the amine N-oxide of about 10:1 to about 1:1000000. However the amount of amine oxide groups present in the polyamine N-oxide containing polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from about 2:3 to about 1:1000000. More preferably from about 1:4 to about 1:1000000, most preferably from about 1:7 to about 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $PKa < 10$, preferably $PKa < 7$, more preferred $PKa < 6$.

The polyamine N-oxide containing polymer can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight of the polyamine N-oxide containing polymer is within the range of about 500 to about 1000,000; preferably from about 1,000 to about 50,000, more preferably from about 2,000 to about 30,000, most preferably from about 3,000 to about 20,000.

Such polymers having a net cationic charge include polyvinylpyrrolidone (PVP) as well as copolymers of N-vinylimidazole N-vinyl pyrrolidone, having an average molecular weight range in the range about 5,000 to about 100,000, preferably about 5,000 to about 50,000; said copolymers having a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from about 1 to about 0.2, preferably from about 0.8 to about 0.3.

Surfactant/Concentration Aids

Although as stated before, relatively concentrated compositions of the unsaturated material of Formula (I) and (II) above can be prepared that are stable without the addition of concentration aids, the concentrated compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients.

Surfactant concentration aids are typically selected from the group consisting of single long chain alkyl cationic surfactants; nonionic surfactants; amine oxides; fatty acids; or mixtures thereof, typically used at a level of from 0 to about 15% of the composition.

Such mono-long-chain-alkyl cationic surfactants useful in the present invention are, preferably, quaternary ammonium salts of the general formula :

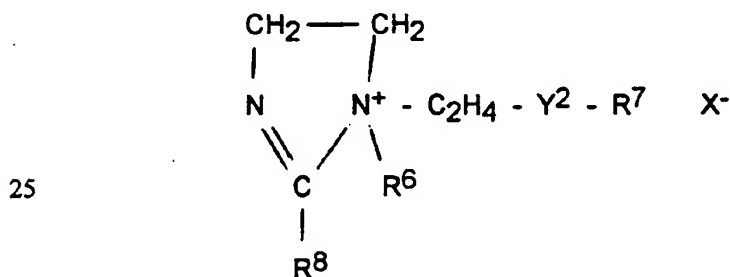


5 wherein the R^2 group is C_{10} - C_{22} hydrocarbon group, preferably C_{12} - C_{18} alkyl group of the corresponding ester linkage interrupted group with a short alkylene (C_1 - C_4) group between the ester linkage and the N, and having a similar hydrocarbon group, e.g., a fatty acid ester of choline, preferably C_{12} - C_{14} (coco) choline ester and/or C_{16} - C_{18} tallow choline
10 ester at from about 0.1% to about 20% by weight of the softener active. Each R is a C_1 - C_4 alkyl or substituted (e.g., hydroxy) alkyl, or hydrogen, preferably methyl, and the counterion X^- is a softener compatible anion, for example, chloride, bromide, methyl sulfate, etc.

Other cationic materials with ring structures such as alkyl
15 imidazoline, imidazolinium, pyridine, and pyridinium salts having a single C_{12} - C_{30} alkyl chain can also be used. Very low pH is required to stabilize, e.g., imidazoline ring structures.

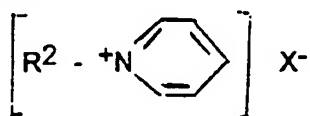
Some alkyl imidazolinium salts and their imidazoline precursors useful in the present invention have the general formula :

20



wherein Y^2 is $-\text{C}(\text{O})-\text{O}-$, $-\text{O}-(\text{O})\text{C}-$, $-\text{C}(\text{O})-\text{N}(\text{R}^5)-$, or
30 $-\text{N}(\text{R}^5)-\text{C}(\text{O})-$ in which R^5 is hydrogen or a C_1 - C_4 alkyl radical; R^6 is a C_1 - C_4 alkyl radical or H (for imidazoline precursors); R^7 and R^8 are each independently selected from R and R^2 as defined hereinbefore for the single-long-chain cationic surfactant with only one being R^2 .

Some alkyl pyridinium salts useful in the present invention have the
35 general formula :

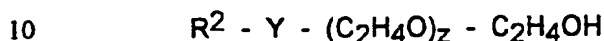


wherein R^2 and X- are as defined above. A typical material of this type is cetyl pyridinium chloride.

Nonionic Surfactant (Alkoxylated Materials)

Suitable nonionic surfactants for use herein include addition
 5 products of ethylene oxide and, optionally, propylene oxide, with fatty alcohols, fatty acids, fatty amines, etc.

Suitable compounds are substantially water-soluble surfactants of the general formula :



wherein R^2 is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups; primary, secondary and branched chain alkenyl hydrocarbyl groups; and
 15 primary, secondary and branched chain alkyl- and alkenyl-substituted phenolic hydrocarbyl groups; said hydrocarbyl groups having a hydrocarbyl chain length of from 8 to 20, preferably from 10 to 18 carbon atoms.

Y is typically -O-, -C(O)O-, -C(O)N(R)-, or -C(O)N(R)R-, in which R^2 and R, when present, have the meanings given hereinbefore, and/or R
 20 can be hydrogen, and z is at least 8, preferably at least 10-11.

The nonionic surfactants herein are characterized by an HLB (hydrophilic-lipophilic balance) of from 7 to 20, preferably from 8 to 15.

Examples of particularly suitable nonionic surfactants include Straight-Chain, Primary Alcohol Alkoxylates such as tallow alcohol-EO(11),
 25 tallow alcohol-EO(18), and tallow alcohol-EO(25);

Straight-Chain, Secondary Alcohol Alkoxylates such as 2-C₁₆EO(11); 2-C₂₀EO(11); and 2-C₁₆EO(14);

Alkyl Phenol Alkoxylates, such as p-tridecylphenol EO(11) and p-pentadecylphenol EO(18), as well as

30 Olefinic Alkoxylates, and Branched Chain Alkoxylates such as branched chain primary and secondary alcohols which are available from the well-known "OXO" process.

Amine Oxides

Suitable amine oxides include those with one alkyl or hydroxyalkyl moiety of 8 to 28 carbon atoms, preferably from 8 to 16 carbon atoms, and two alkyl moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups with 1 to 3 carbon atoms.

Examples include dimethyloctylamine oxide, diethyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecyl-amine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dimethyl-2-hydroxyoctadecylamine oxide, and coconut fatty alkyl dimethylamine oxide.

Fatty Acids

Suitable fatty acids include those containing from 12 to 25, preferably from 16 to 20 total carbon atoms, with the fatty moiety containing from 10 to 22, preferably from 10 to 14 (mid cut), carbon atoms. The shorter moiety contains from 1 to 4, preferably from 1 to 2 carbon atoms.

Electrolyte Concentration Aids

Inorganic viscosity control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition.

Alkylene polyammonium salts can be incorporated into the composition to give viscosity control in addition to or in place of the water-soluble, ionizable salts above. In addition, these agents can act as scavengers, forming ion pairs with anionic detergent carried over from the main wash, in the rinse, and on the fabrics, and may improve softness performance. These agents may stabilize the viscosity over a broader

range of temperature, especially at low temperatures, compared to the inorganic electrolytes.

Specific examples of alkylene polyammonium salts include L-lysine monohydrochloride and 1,5-diammonium 2-methyl pentane dihydrochloride.

Liquid Carrier.

Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier employed in the instant compositions is preferably at least primarily water due to its low cost relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least about 50%, most preferably at least about 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <about 200, organic solvent, e.g., lower alcohol such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols include monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

Still other optional ingredients are stabilizers, such as well known antioxidants and reductive agents, Soil Release Polymers, bacteriocides, colorants, perfumes, preservatives, optical brighteners, anti ionisation agents, antifoam agents, and the like.

EXAMPLES 1-3:

The following concentrated compositions are prepared :

5	<u>Ingredients</u>	<u>Example 1</u> % by weight	<u>Example 2</u> % by weight	<u>Example 3</u> % by weight
	N,N-di(2-tallowoxyl-oxy-ethyl)- N,N-dimethyl ammonium chloride IV=18	23%	23%	23%
10	Tallowalcohol ethoxylated 25 time	2%	2%	2%
	Polyglycerolmonostearate	3.5%	3.5%	3.5%
	Cellulase* CEVU/g of composition	8.50	67	67
	Hydrochloric acid	0.08%	0.08%	0.08%
	PVNO**	-	-	0.5%
15	Polyethylene glycol MW:4000	0.6%	0.6%	0.6%
	Calcium chloride	0.3%	0.3%	0.3%
	Perfume	0.9%	0.9%	0.9%
20	Dye, antifoam, water, minors	Balance to 100%	Balance to 100%	Balance to 100%

pH (neat) = 2.3

* Most preferred cellulases are those as described in International Patent Application WO91/17243, incorporated herein by reference in its entirety. For example, a cellulase preparation useful in the compositions of the invention can consist essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from Humicola insolens, DSM 1800, or which is homologous to said 43kD endoglucanase.

** PVNO = poly(vinylpyridine N-oxide).

The formula of Example 1 is used in the typical European machine washing process to clean fabrics, especially cotton fabrics, by addition of 35g of this composition to the rinse cycle of this process which uses 21 liters of water for the rinse solution (14 CEVU's of cellulase per liter of rinse solution) to provide cleaned fabrics having noticable fabric benefits.

The formulas of Examples 2 and 3 are used in the typical U.S. machine washing process to clean fabrics by addition of 30g of this

composition to the rinse cycle of this process which uses 64 liters of water for the rinse solution (31 CEVU's of cellulase per liter of rinse solution) to provide cleaned fabrics having noticable fabric benefits.

EXAMPLE 4

5 The following concentrated composition is also prepared :

	Ingredients	Example 4 (% by weight)
10	N,N-di(2-tallowoxyl-oxy-ethyl)- N,N-dimethyl ammonium chloride IV=55	26%
	Cellulase* CEVU/g of composition	80
	Hydrochloric acid	0.08%
	Perfume	1.35%
	Calcium chloride	0.60%
15	Dye, antifoam, water and minors	balance to 100

pH (neat) = 3.2

20 * Most preferred cellulases are those as described in International Patent Application WO91/17243. For example, a cellulase preparation useful in the compositions of the invention can consist essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from Humicola insolens, DSM 1800, or which is homologous to said 43kD endoglucanase.

25

The formula of Example 4 is used in the typical U.S. machine washing process to clean fabrics by addition of 30g of this composition to the rinse cycle of this process which uses 64 liters of water for the rinse solution (37 CEVU's of cellulase per liter of rinse solution) to provide
30 cleaned fabrics having noticable fabric benefits. Benefits are also observed for the composition of Example 4 containing cellulase having 40 CEVU's/g of composition activity under these conditions (19 CEVU's of cellulase per liter of rinse solution).

EXAMPLE 5

35 The following dilute composition is also prepared :

	Ingredients	Example 5 (% by weight)
5	N,N-di(2-tallowoxyl-oxy-ethyl)- N,N-dimethyl ammonium chloride IV=18	5.5%
	Tallowalcohol ethoxylated 25 times	0.4%
	Polyglycerolmonostearate	0.8%
	Cellulase* CEVU/g of composition	3.5
	Hydrochloric acid	0.04%
10	Perfume	0.25%
	Benzoic Acid	0.3%
	Dye and water	balance to 100

pH (neat) = 2.3

* Most preferred cellulases are those as described in International Patent Application WO91/17243. For example, a cellulase preparation useful in the compositions of the invention can consist essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from Humicola insolens, DSM 1800, or which is homologous to said 43kD endoglucanase.

The formula of Example 5 is used in the typical U.S. machine washing process to clean fabrics by addition of 100g of this composition to the rinse cycle of this process which uses 64 liters of water for the rinse solution (5 CEVU's of cellulase per liter of rinse solution) to provide cleaned fabrics having noticable fabric benefits.

EXAMPLE 6

The following concentrated composition is also prepared :

	Ingredients	Example 6 (% by weight)
30	Ditallow Dimethyl Ammonium Chloride	10%
	Varisoft 222*	14.5%
	Cellulase** CEVU/g of composition	80
35	Hydrochloric acid	trace
	Perfume	1.0%
	Calcium chloride	0.3%
	Dye, water and minors	balance to 100

pH (neat) = 5.6

* Methyl bis(tallowamidoethyl)(2-hydroxyethyl) ammonium methyl sulfate sold by Witco Chemical Company.

- 5 ** Most preferred cellulases are those as described in International Patent Application WO91/17243. For example, a cellulase preparation useful in the compositions of the invention can consist essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from
- 10 Humicola insolens, DSM 1800, or which is homologous to said 43kD endoglucanase.

- 15 The formula of Example 6 is used in the typical U.S. machine washing process to clean fabrics by addition of 30g of this composition to the rinse cycle of this process which uses 64 liters of water for the rinse solution (37 CEVU's of cellulase per liter of rinse solution) to provide cleaned fabrics having noticable fabric benefits.

What is Claimed is:

1. A fabric conditioning composition comprising one or more cationic fabric softening agents, nonionic fabric softening agents, or mixtures thereof, and a cellulase, said composition having cellulase present at a level such that the composition delivers an effective amount of cellulase below 50 CEVU's per liter of rinse solution during machine rinse cycle use conditions.
2. A composition according to Claim 1 comprising cellulase at a level equivalent to an activity from 5 to 125 CeVU/gram of composition.
3. A composition according to either of Claims 1 or 2 comprising cellulase at a level such that the composition delivers an effective amount of cellulase below 30 CEVU's per liter of rinse solution during machine rinse cycle use conditions.
4. A composition according to any of Claims 1-3 wherein the cellulase consists essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from Humicola insolens, DSM 1800, or which is homologous to said 43kD endoglucanase.
5. A composition according to any of Claims 1-4 comprising from 2% to 50% by weight of one or more fabric softening agents.
6. A fabric softening composition according to any of Claims 1-5 comprising a quaternary ammonium softening agent, amine precursor softening agent, or mixtures thereof, and a cellulase, and, if desired, conventional matrix components and additives, and that the composition has a neat pH, at 20°C, of from 2.0 to 4.5.
7. A composition according to Claim 6 wherein the quaternary ammonium softening agent is N,N-di(2-tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride.

8. A process for machine treatment of fabrics, said process comprising treating fabric during the rinse cycle of a machine washing process with one or more cationic fabric softening agents, nonionic fabric softening agents, or mixtures thereof, and cellulase at a level below 50 CEVU's per liter of rinse solution.

9. A process according to Claim 8 wherein the cellulase is at a level below 30 CEVU's per liter of rinse solution.

10. A process according to either of Claims 8 or 9 wherein the cellulase consists essentially of a homogeneous endoglucanase component, which is immunoreactive with an antibody raised against a highly purified 43kD cellulase derived from Humicola insolens, DSM 1800, or which is homologous to said 43kD endoglucanase.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/08893

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/00 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,91 13136 (NOVO NORDISK A/S) 5 September 1991 cited in the application see page 4, line 23 - page 5, line 27; claims; example 5 ---	1-5,8-10
P,X	TENSIDE, vol.30, no.6, December 1993, MUNICHEN DE pages 388 - 393, XP415632 U. HOTZ 'Verwendung von Cellulasen in Waschmitteln' see page 390, paragraph 2 - page 393 ---	1-5
A	---	8-10
A	EP,A,0 173 397 (UNILEVER NV.) 5 March 1986 see the whole document ---	1-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

20 December 1994

Date of mailing of the international search report

10.01.95

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 94/08893

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 495 554 (THE PROCTER & GAMBLE COMPANY) 22 July 1992 see the whole document ---	1-10
A	EP,A,0 239 910 (THE PROCTER & GAMBLE COMPANY) 7 October 1987 see the whole document ---	7
A	GB,A,2 258 655 (SANDOZ LTD.) 17 February 1993 see the whole document ---	6
P,A	WO,A,94 03577 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 17 February 1994 see page 5, paragraph 2 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 94/08893

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9113136	05-09-91	DE-D- 69100751	20-01-94
		DE-T- 69100751	24-03-94
		DE-D- 69101219	24-03-94
		DE-T- 69101219	01-06-94
		WO-A- 9113141	05-09-91
		WO-A- 9113142	05-09-91
		EP-A- 0517761	16-12-92
		EP-A- 0517762	16-12-92
		ES-T- 2051122	01-06-94
		ES-T- 2047400	16-02-94
		JP-T- 5504367	08-07-93
		JP-T- 5504368	08-07-93
EP-A-0173397	05-03-86	AU-B- 558229	22-01-87
		AU-A- 4664785	06-03-86
		CA-A- 1239602	26-07-88
		DE-A- 3583713	12-09-91
		JP-A- 61064797	03-04-86
		US-A- 4661289	28-04-87
EP-A-0495554	22-07-92	AU-A- 1230592	27-08-92
		AU-A- 1542092	27-08-92
		BR-A- 9205428	05-04-94
		CA-A- 2099508	17-07-92
		CA-A- 2100097	17-07-92
		CA-A- 2100554	17-07-92
		CN-A- 1064309	09-09-92
		CZ-A- 9301410	16-03-94
		EP-A- 0495257	22-07-92
		EP-A- 0495258	22-07-92
		HU-A- 65221	02-05-94
		JP-T- 6504311	19-05-94
		JP-T- 6505049	09-06-94
		JP-T- 6509122	13-10-94
		NZ-A- 241308	26-07-94
		WO-A- 9213054	06-08-92
		WO-A- 9213053	06-08-92
		WO-A- 9213057	06-08-92
EP-A-0239910	07-10-87	GB-A- 2188653	07-10-87

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 94/08893

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0239910		AU-B- 599966	02-08-90
		AU-A- 7096587	08-10-87
		CA-A- 1279448	29-01-91
		DE-A- 3782075	12-11-92
		JP-A- 63006168	12-01-88
		US-A- 4767547	30-08-88

GB-A-2258655	17-02-93	DE-A- 4226162	18-02-93
		ES-A- 2048666	16-03-94
		FR-A- 2680372	19-02-93
		JP-A- 5207878	20-08-93

WO-A-9403577	17-02-94	DE-A- 4224947	03-02-94
		DE-A- 4236698	05-05-94
